

# PATENT SPECIFICATION

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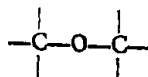
## (54) IMPROVEMENTS IN OR RELATING TO POLYURETHANE FOAMS AND TO A METHOD OF PRODUCING SAME

(71) We, ELEKAL, a French body corporate, of 43 rue Vincuse, Paris 16e, France, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a flexible and hydrophilic polyurethane foam and to a method of making the same.

As is known, polyurethane foams, in particular flexible polyurethane foams, are made by reacting a polyether based polyol with a polyisocyanate in the presence of water, a catalyst and a surface active agent. The catalysts normally used are divalent tin salts of fatty acids and tertiary amines, whilst the surface active agent used is normally a silicon oil.

Polyether based polyols are macromolecular chain polyols having one or more etheroxide linkages:



Examples of such polyether based polyols are diols terminated by primary hydroxyl groups, in particular polyethylene glycol and polypropylene glycol, and triols or polyalcohols having more than three hydroxyl groups produced by reacting ethylene oxide or propylene oxide with compounds having active hydrogen atoms, such as polyols and polyamines. Examples of such polyols are those known by the registered Trade Marks "Niax" and "Voranol".

A variety of polyisocyanates can be used to make the polyurethane foams. Use can also be made of mixtures of polyisocyanates. Those most commonly used are diisocyanates, in particular, a mixture of 2,4-tolylene-diisocyanate and 2,6-tolylene-diisocyanate.

The properties of the resulting polyurethane foams vary, depending on the chemical nature of the polyols and of the polyisocyanates that are used, and on the porous structure of the foam which depends on the chemical nature of its constituents.

An important application for flexible polyurethane foams lies in sponges used in particular for household and cleaning purposes. The essential quality which such sponges must have is good water absorption as this determines their wiping properties. The extent to which flexible polyurethane foams can absorb water mainly depends on the nature of the polyol or polyols used in their preparation. It has been found that polyethylene glycol, which has an inherently great affinity for water since it is soluble in water whatever its molecular weight, tends to increase the hydrophilic properties of the foam whereas polypropylene glycol has a tendency to decrease these hydrophilic properties.

The chemical structure of the foam also has an important bearing on the hydrophilic properties of the latter: the long linear sections resulting from the polyol can include hydrophilic zones, e.g. polyoxyethylene units, and hydrophobic zones, e.g. polyoxypropylene units. The relative arrangement of these zones, both to each other and to the sections of the molecules which result from the polyisocyanate and which

polyether-diol was liquid and viscous at ordinary temperature, and its main characteristic properties were as follows:

$$I_{OH}=46$$

Molecular weight: 2460 (theoretical molecular weight: 2514)

Average number of attached propylene oxide units:  $x+z=18$

#### Polyether-diol I

Into a three-necked 5-litre flask provided with a mechanical stirring device, a thermometer and a double-walled pear-shaped tapped funnel, and maintained under nitrogen atmosphere, at atmospheric pressure, there was poured 1 kg of polyethylene glycol having an average molecular weight of 600 (PEG 600) and a hydroxyl index of 187 ( $I_{OH}=187$ ). At the same time 40 g of a 40% solution of benzyl trimethyl ammonium hydroxide in methanol and 1 g of hydroquinone (for oxidation inhibiting purposes) were poured into the flask. Thereafter, 900 g of propylene oxide was progressively added dropwise over a period of 36 hours. The reaction was slightly exothermic. The temperature of the flask was kept during addition of the propylene oxide at between 60 and 80°C.

1600 g of a polyether-diol whose main characteristic properties are as follows was produced:

$$I_{OH}=113$$

Molecular weight: 1000 (theoretical molecular weight: 996)

Average number of propylene oxide units:  $x+z=7$

#### Polyether-diol V

The procedure was the same as that of the preparation of Polyether-diol I, using 680 g (850 cc) of propylene oxide and 1000 g of PEG 1450. After reacting for 36 hours at 80°C, 1450 of a polyether-diol whose main characteristic features are as follows was produced:

$$I_{OH}=71$$

Molecular weight: 1580 (theoretical molecular weight: 1586)

Average number of propylene oxide units:  $x+z=2$

Melting point: 37°C.

#### Polyether-diol VII

The procedure was the same as that of preparation of Polyether-diol I, using 30 g of propylene oxide, 200 g of PEG 2000 and 3 g of potassium hydroxide. After reacting for 20 hours at 80°C, there was produced 223 g of a polyether-diol which was a viscous liquid at 25°C and whose main characteristic properties were as follows:

$$I_{OH}=50.7$$

Molecular weight: 2230 (theoretical molecular weight: 2230)

Average number of propylene oxide units:  $x+z=4$

#### EXAMPLE 1

There was prepared, by stirring with a rotary stirrer turning at 3500 rpm, an intimate mixture of:

Niax L-56 (primary polyether triol made by Union Carbide)

Mixed polyether-diol I

SF 1066 Silicone oil (General Electric)

Water

Stannous octoate

Bis(2-dimethylaminoethyl ether)

C-2-0145 Silicone (Siss)

Yellow Neozapon R dyestuff (BASF)

90 parts

10 parts

2 parts

3.5 parts

0.1 parts

0.5 parts

0.005 parts

0.2 parts

Mixture of  $\left\{ \begin{array}{l} 80 \text{ mole \% of 2,4-tolylenediisocyanate} \\ 20 \text{ mole \% of 2,6-tolylene diisocyanate} \end{array} \right\}$  TDI index 105

These substances were added in the given order, to the reaction mixture, their temperature upon introduction being 22°C. After introducing the tolylene diisocyanate mixture, stirring was continued for at most 10 seconds, whereupon the contents of the stirrer were poured into a mould and the foam left to rise, this being complete after about one minute. The foam was then kept in an oven at 80°C for about one hour.

The resulting foam had a markedly hydrophilic nature which was quantitatively evaluated by measuring the "wiping efficiency", i.e. the extent to which water can be wiped off by a standard size sponge of 14×9×5 cm. For this purpose, 50 cc of water was uniformly spread over a smooth square surface of 50×50 cm. Wiping was then carried out with both faces of the sponge for 25 seconds. The "wiping efficiency" is the percentage of water absorbed in relation to the initial amount of water. The wiping efficiency of foam was 89%, and its capillary absorption efficiency, as defined in French Patent Specification No. 1,284,015 (Rhône-Poulenc), was 70%.

By way of comparison, a foam was prepared as described above using the following constituents:

Niax L-56	100 parts
SF 1066 Silicone oil	2 parts
Water	3.5 parts
Stannous octoate	0.1 parts
Bis(2-dimethylaminoethyl ether)	0.5 parts
C-2-0145 Silicone	0.005 parts
Yellow Neozapon R dyestuff	0.2 parts

Mixture of  $\left\{ \begin{array}{l} 80 \text{ mole } \% \text{ of 2,4-tolylene diisocyanate} \\ 20 \text{ mole } \% \text{ of 2,6-tolylene diisocyanate} \end{array} \right\}$  TDI index: 105

The hydrophilic properties of the foam were as follows:

Wiping efficiency (W.E.): 44%  
Capillary absorption efficiency (C.A.E.): 12%

#### EXAMPLE 2

The procedure described in Example 1 was repeated, using the following constituents:

Niax 14-46 (Union Carbide)	50 parts
Mixed polyether-diol II	50 parts
Stannous octoate	0.15 parts

The other constituents were the same as in Example 1. The resulting foam had a wiping efficiency of 91% and a capillary absorption efficiency of 74.6%.

For comparison, a foam was prepared in the same manner using the following constituents:

Niax 14-46	100 parts
SF 1066 Silicone oil	2 parts
Water	3.5 parts
Stannous octoate	0.15 parts
Bis(2-dimethylaminoethyl ether)	0.5 parts
C-2-0145 Silicone	0.005 parts
Yellow Neozapon R dyestuff	0.2 parts

Mixture of  $\left\{ \begin{array}{l} 80 \text{ mole } \% \text{ of 2,4-tolylene diisocyanate} \\ 20 \text{ mole } \% \text{ of 2,6-tolylene diisocyanate} \end{array} \right\}$  TDI index 105

The hydrophilic properties of the foam were as follows:

W.E. = 76%  
C.A.E. = 40%

those having ordinary skill in the art without departing from the spirit and scope of the present invention.

What is claimed is:

1. A method of preparing a superabsorbent polyurethane foam which comprises mixing an isocyanate-terminated polyurethane prepolymer having an isocyanate functionality greater than two with an aqueous solution of at least one first compound in the presence of at least one thermally activated free radical initiator and at least one second compound, said at least one first compound having (1) at least one carbon-carbon double bond capable of undergoing addition polymerization with the at least one second compound and with itself and other first compounds which may be present and (2) at least one functional group selected from the group consisting of carbamoyl, substituted carbamoyl, and carboxy and the alkali metal and ammonium salts thereof; said second compound having at least two carbon-carbon double bonds which are capable of undergoing addition polymerization with said at least one first compound; the proportion of said first and second compounds are selected to impart superabsorbent properties to the resulting polyurethane foam; and the resulting polyure-

thane foam is essentially free of grafting of addition polymer to polyurethane.

2. The method of claim 1, in which said polyurethane prepolymer is an isocyanate-terminated poly(oxyalkylene) polyol.

3. The method of claim 2, in which said polyurethane prepolymer has an isocyanate functionality equal to or greater than about 2.3.

4. The method of claim 1, in which said at least one first compound is selected from the group consisting of amides, alkali metal salts, and ammonium salts of acrylic and methacrylic acid.

5. The method of claim 4, in which said at least one first compound is selected from the group consisting of acrylamide and potassium acrylate.

6. The method of claim 1, in which said at least one second compound is selected from the group consisting of acrylamides, methacrylamides, and esters of acrylic and methacrylic acid with aliphatic polyols.

7. The method of claim 6, in which said at least one second compound is selected from the group consisting of methylene-bis-acrylamide and 1,6-hexanediol diacrylate.

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